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1 **Liquid-liquid transition and critical point in sulfur**

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10 **A liquid-liquid transition (LLT) is a peculiar phenomenon in which a single-**
11 **component liquid transforms into another one via a first-order phase transition. Due**
12 **to their counterintuitive nature, LLTs have intrigued scientists for several years and**
13 **changed our perception of the liquid state. Such LLTs have been predicted from**
14 **computer simulations of water^{1,2}, silicon³, carbon dioxide⁴, carbon⁵, hydrogen⁶ and**
15 **nitrogen⁷. Experimental evidence has been mostly found in supercooled, i.e.**
16 **metastable, liquids such as Y₂O₃–Al₂O₃ mixtures⁸, water⁹ and other molecular**
17 **liquids^{10,11,12}, but the LLT in supercooled liquids often occurs simultaneously with**
18 **crystallization, making it hard to separate the two phenomena¹³. A liquid-liquid**
19 **critical point (LLCP), similar to the gas-liquid critical point, has been predicted at**
20 **the end of the LLT line in some cases, but so far never experimentally observed for**
21 **any materials. This putative LLCP has for instance been invoked in the case of water**
22 **to understand its thermodynamic anomalies¹. Here we report combined *in-situ***
23 **density measurements, x-ray diffraction and Raman scattering that provide direct**
24 **evidence for a first-order liquid-liquid transition and a liquid-liquid critical point in**
25 **sulfur. The transformation manifests itself by a sharp density jump between the low**

26 **and high density liquids, and distinct features in the pair distribution function. A**
27 **non-monotonic variation of the density jump with temperature is observed, which**
28 **first increases on moving away from the critical point and then decreases. This**
29 **behavior is linked to competing effects of density and entropy in driving the**
30 **transition.**

31 The pressure (P)-temperature (T) phase diagram of sulfur exhibits important
32 similarities with that of phosphorus which is to date the only element for which a direct
33 *in-situ* observation of a LLT has been unambiguously evidenced^{14,15,16}. The stable sulfur
34 solids at room P, α - and β -sulfur^{17,18}, consist of S₈ molecules, while at high P-T, the stable
35 polymorph is a polymeric solid composed of helical chains¹⁹. At room P the molecular
36 character is conserved in the liquid upon melting at 388 K and up to 432 K where the so-
37 called “lambda transition” (λ -T) occurs²⁰. The λ -T has been described as a “living”
38 polymerization transition²¹, reversible and incomplete (the polymer content reaches a
39 maximum of ~60% at the boiling point, T=718 K), where a fraction of the S₈ cyclic
40 molecules open up and coalesce into long polymeric chains or rings. It is associated with
41 a large increase in viscosity and an anomalous but not discontinuous density variation^{20,22}.
42 For P above 5 GPa and T above 1000 K, several P-T domains with different thermal and
43 electrical properties have been proposed in liquid sulfur²³. An experimental study²⁴
44 suggested the existence above 6 GPa of a purely polymeric liquid composed of long
45 chains below 1000 K, which split to shorter chains at higher temperature. *Ab-initio*
46 molecular dynamics simulations²⁵ reproduced this chain breakage in the compressed
47 liquid but found no discontinuous change of density associated to this process. So far, no
48 *in-situ* structural or vibrational studies have been conducted in the pressure region below
49 3 GPa in the mixed molecular-polymeric liquid.

50 We performed *in-situ* x-ray absorption, x-ray diffraction and Raman scattering at
51 the beamline ID27 of the European Synchrotron Radiation Facility (ESRF)²⁶ to probe the
52 density, structure and dynamics evolution of liquid sulfur in the P-T domain 0-3 GPa,
53 300-1100 K (see Supplementary Information S1-S3 for methods). The P-T paths are
54 represented in the experimental phase diagram of sulfur in Fig. 1.

55

56 **Figure 1**

57 Density measurements were obtained in the Paris-Edinburgh press along eight
58 isothermal (P1 to P8 in Fig. 1) and two isobaric pathways (P9 and P10). The accuracy of
59 the density measured by this method is of the order of 1% (Supplementary Information
60 S1). XRD patterns of the sample were also collected at each P-T point to confirm that the
61 sample was fully molten. As shown in Fig. 2a, along isothermal pathways P1-P5 below
62 1000 K, we systematically observed a discontinuous jump in density over a very narrow
63 pressure domain of ~ 0.07 GPa, strongly suggesting the existence of a first-order phase
64 transition between a low (LDL) and a high density liquid (HDL). Discontinuous density
65 shifts were also observed upon varying the temperature at constant load along pathways
66 P9-P10 (Supplementary Figure S9). These density jumps were accompanied by sudden
67 changes in the structure factor $S(Q)$ of the sulfur melt, as shown in Fig. 2b. This is
68 particularly apparent on the width and position of the first diffraction peak which abruptly
69 change at the transition. The density variation estimated from the measured $S(Q)$ using
70 the methodology of Ref. [27] (see Supplementary Information S3) very well compares
71 with that derived from the x-ray absorption measurements (see inset of Fig. 2c), giving
72 an independent confirmation of the discontinuous density jump at the transition.

73 Fig. 2c presents x-ray radiographic images taken along a compression pathway at
74 980 K and pressures between 1.6 and 2.5 GPa. These images show that below (panel *i*)
75 and above (panel *iv*) the transition, the sample is homogeneous, while at the transition an
76 interface separating a “bubble” of HDL from the surrounding LDL appears (panels *ii* and
77 *iii*). As seen in the Supplementary video 1, the HDL bubble grows as the load is increased
78 until the sample is fully in the HDL phase. These observations provide a compelling
79 evidence of a coexistence of the LDL and HDL phases at the transition, and together with
80 the density and structure factor measurements, confirm the first-order nature of the liquid-
81 liquid transition.

82 At 1090 K and 1100 K (pathways P7 and P8 in Fig. 1), we did not observe, within
83 uncertainties, any discontinuous shift of the density as a function of pressure thus
84 indicating the presence of a liquid-liquid critical point (LLCP). The LLCP was likely
85 crossed along the pathway P6 at ~ 2.15 GPa and 1035 K (indicated by a star in Fig. 2a)
86 where the density measurements show clear anomalies (see Supplementary Information
87 S2), while at lower and higher pressures along this isotherm, the density appears to
88 continuously vary with pressure. As shown in Fig. 2d, we observe a non-monotonic
89 evolution of the density discontinuity with temperature: starting from zero at the LLCP,
90 it first increases to reach a maximum of $\sim 7.5\%$ at about 750 K and then decreases.

91 **Figure 2**

92 Fig. 3a shows the pair distribution function (PDF) $g(r)$ obtained by Fourier
93 transform of the measured $S(Q)$ at 5 selected points along the P8 pathway: A, B and C
94 are in the LDL domain, while D and E are in the HDL domain, close to the LDL-HDL
95 transition line (see Fig. 1). The LDL PDF at point A (0.11 GPa, 428 K) is very similar to
96 those reported for the ambient-pressure molecular liquid below the lambda transition^{28,29}.

97 It displays three well-defined peaks at 2.05, 3.39(2) and 4.45(2) Å, in very good
98 agreement with the previous cited works. As shown in the latter, the third peak is a
99 fingerprint of the S₈ molecule since it occurs at the average distance of the third and fourth
100 neighbors in a S₈ ring, as deduced from the structure of the molecular α-sulfur crystal.
101 When the temperature is increased in the LDL domain above the lambda transition (points
102 B at 0.17 GPa-442 K, and C at 0.36 GPa-487 K), the observed evolution is also very
103 similar to that described in the literature for the ambient-pressure liquid²⁸. Namely, the
104 positions and intensities of the first and second-neighbor peaks are weakly affected,
105 whereas the third peak strongly reduces in intensity and becomes bi-modal. These
106 changes in the third/fourth neighbor distribution are a signature of the rapid increase of
107 polymer content and associated reduction of the S₈ content above the lambda transition.
108 Indeed, the peak at 4.45 Å, characteristic of S₈ molecules, reduces in intensity and a new
109 component at 4 Å appears and grows with temperature, originating from the formation of
110 long polymeric chains or rings. The similarities between the present PDF in the region
111 from 4 to 5 Å and those reported by Bellissent et al.²⁸ from ambient-pressure neutron
112 diffraction can be appreciated from the comparison of the inset of Fig. 3a and Fig. 3b. We
113 note however that the new component in the ambient pressure PDF appears at a larger
114 distance, around 4.2 Å, which is likely due to the lower density of the ambient pressure
115 liquid.

116 **Figure 3**

117

118 We now come to the structural modifications in the PDF across the LDL-HDL
119 transition. As seen in Fig. 3c and S15, no change, within uncertainties, occurs on the first
120 and second peak positions, showing that the S-S bond length and the <S-S-S> angle are

121 the same as in the LDL. The most important modifications occur again in the third/fourth-
122 neighbour distributions. The bi-modal shape of the third peak is maintained but the
123 component at 4.45 Å is even more reduced, and the component located at 4 Å in the LDL
124 undergoes a sudden shift in position to 4.15 Å in the HDL. This shows that the local order
125 in the liquid changes at the transition, and further, suggests that the polymer content in
126 the HDL is larger than in the LDL. The latter point is confirmed by the comparison of the
127 Raman spectra measured in the LDL and HDL shown in Fig. 3d. In the HDL domain, we
128 observe an intensity increase of the stretching mode at 460 cm⁻¹ assigned to the polymeric
129 chains³⁰, concomitant with a drop of the molecular bending mode at 152 cm⁻¹ and
130 breathing mode at 220 cm⁻¹ of the S₈ molecule, attesting that the latter are residual in the
131 HDL region.

132 This work thus demonstrates that sulfur undergoes a first-order phase transition
133 between two thermodynamically stable liquids, with clear experimental evidence of a
134 sharp density increase and structural modifications. We stress that this LLT is distinct
135 from the long-known lambda transition, which is associated to second-order like changes
136 in density^{20,22} and heat-capacity³¹. Furthermore, the lambda transition temperature slowly
137 decrease with pressure³² whereas for the present LLT, the transition temperature increases
138 with pressure (see also Supplementary Information S4). By virtue of the Clapeyron
139 equation, and since a positive jump of density occurs at the transition, this tells us that the
140 entropy of the HDL is smaller than that of the LDL, which contrasts with the entropy
141 increase in the LDL at the lambda transition³³. The entropy reduction across the LLT may
142 be due in part to the increase in polymer content revealed by present experiments, and
143 associated reduction in the mixing entropy. But the observed changes in the PDF also
144 indicate that the local conformation of neighbor polymeric units is modified, certainly to

145 a more compact arrangement imposed by the density increase, leading to a reduction in
146 the conformation entropy as well.

147 The shape of the transition line and the presence of a critical point make this LLT
148 in sulfur strongly resemble the well-known liquid-gas transition (LGT). However, there
149 is an important difference, which is the non-monotonic variation of the density jump with
150 temperature of the LLT, which first increases from zero as the temperature is decreased
151 from the LLCP and then decreases, contrasting with the monotonic increase of density
152 along the LGT transition. Such a behavior was recently predicted by AIMD calculations
153 along the LLT line of phosphorus³⁴, from which the authors suggested that the order
154 parameter describing the LLT contains contributions from both the density and entropy,
155 and that at least at low temperatures, entropy governs the transition rather than density.
156 This is at odds with the LGT where density is the sole order parameter. A two-order
157 parameters model including density, on one hand, and a bond-order parameter describing
158 locally favoured structures, on the other hand, was also proposed by Murata and Tanaka¹³
159 to explain the existence of LLTs. The putative LLT in water has also been described as
160 entropy-driven based on a model where water is considered as an “athermal solution” of
161 two molecular structures with different entropies and densities³⁵. We note however that
162 the present LLT in sulfur is different from that in water and phosphorus in the sense that
163 the transition line has a positive slope in sulfur but a negative one in water and
164 phosphorus. This may signal that sulfur belongs to a different class of LLT.

165 This work also provides the first, to the best of our knowledge, experimental
166 evidence for a critical point terminating the line of a LLT. Such a LLCP was proposed in
167 phosphorus at about 3500 K – 0.02 GPa³⁴, conditions which have not yet been achieved
168 by experiment. In supercooled liquid silicon, classical empirical calculations have

169 predicted a LLCPP at negative pressures (-0.6 GPa, 1120 K)³⁶ but *ab-initio* calculations
170 recently determined that the HDL and HDL-vapor spinodals form a continuous reentrant
171 curve, making supercooled Si a critical point free system³⁷. In water, the existence of a
172 LLCPP has been conjectured by Poole in 1992 et al.¹ to explain the many anomalies in the
173 thermodynamic properties such as the heat capacity, compressibility and thermal
174 expansion coefficients, and evidence for this LLCPP has been strongly searched for and
175 debated ever since. The experimental observation of this hypothetical LLCPP in water may
176 well never be possible as it is located in the “no man’s land”, i.e. the P-T domain below
177 the homogeneous nucleation temperature. Finally, a LLCPP has also been predicted in
178 simple molecular systems, such as H₂⁶ and N₂⁷ but their experimental observation remain
179 extremely challenging. The LLCPP in sulfur, being in a P-T range easily accessible by
180 experiment, provides a unique opportunity for the study of critical phenomena associated
181 to LLTs. We thus expect that the present work will spark a new interest in liquid-liquid
182 transitions that will provide a solid basis for understanding the principles that govern
183 LLTs in general. Future works should also focus on deciphering the microscopic
184 processes at the origin of the LLT in sulfur.

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297 **Figure Legends**

298 **Fig. 1. Phase diagram of sulfur around the liquid-liquid transition.** P1 to P8:
 299 isothermal pathways followed during the density measurements presented in Fig. 2. P1,
 300 P2, P4 to P7 were made on compression while P3 (diamond symbols) and P7 (open black
 301 **circles**) were made on decompression. For clarity, P7 and P8 are shown up to 3 GPa only.
 302 P9 and P10 are isobaric pathways followed during the density measurements presented
 303 in Fig. S9 (Supplementary Information S1). The letters A, B, C, D, E (blue filled triangles)
 304 along path P11 indicate the P, T conditions of the selected XRD data in Fig. 3. I, II and
 305 III are the P,T points of the Raman spectra presented in Fig. 3. The black dashed line is
 306 the transition line between the low density liquid (LDL) domain (in yellow) and the high
 307 density liquid (HDL) domain (in pink) that terminates at the critical point **C_p** (black solid
 308 circle).

309 **Fig. 2. First-order liquid-liquid transition in sulfur. a.** Relative pressure variation of
 310 the liquid density ρ/ρ_0 (ρ_0 : density of the lowest pressure point for each isotherm)
 311 collected along seven isothermal pathways (P1, P2 and P4 to P8 in Fig. 1). For clarity,
 312 the density jump obtained on decompression along P3 and along the isothermal paths P9
 313 and P10 are presented in the Extended Data Fig. 1 and 3. Main panel: at T below 1030 K,
 314 a clear density jump is observed along all the isothermal paths. At ~1035 K, a density
 315 anomaly is detected in the vicinity of the LLCP (see Extended Data Fig. 4). Above the
 316 LLCP (inset panel), a continuous variation of the density is observed. **b.** Structure factors
 317 $S(Q)$ of liquid sulfur collected along the isothermal path P2 (T=650 K). The red arrow
 318 emphasizes the shift of the first peak position of $S(Q)$ at the LDL-HDL transition. The
 319 $S(Q)$'s collected on decompression at 740 K are shown in the Extended Data Fig. 2. The
 320 variation of the density calculated from the associated Pair Distribution Function (PDF)
 321 (black filled squares) is presented in the inset panel together with the one obtained from
 322 the direct density measurements (red empty squares). **c.** X-ray radiography of liquid sulfur
 323 across the LDL-HDL transition line at T=980 K and pressures between 1.6 and 2.5 GPa.

324 *i*: Pure LDL, *ii and iii*: LDL-HDL coexistence, *iv*: Pure HDL. The yellow arrow indicates
 325 the LDL-HDL boundary. **d**. Temperature evolution of the density jump. The black and
 326 blue symbols correspond to the isothermal pathways (P1 to P8) and, the red symbols to
 327 the isobaric (P9 and P10) pathways. A maximum of 7.5 % is located at ~750 K.

328 **Fig. 3. Local order in the low- and high-density liquid sulfur.** **a**. The main panel
 329 presents the pair distribution function $g(r)$ of liquid sulfur at selected pressure and
 330 temperature conditions along path P11 of Fig. 1. The letters A to E in parentheses refers
 331 to the P,T conditions in Fig. 1 at which the measurements were performed. The curves
 332 are vertically offset by 0.3 for clarity. The inset shows an enlargement of the PDF in the
 333 region from 0.4 to 0.5 nm which contains contributions from third and fourth neighbours.
 334 **b** shows an enlargement of the third peak of $G(r)$ from the ambient-pressure neutron data
 335 of Ref. 28 at 423 K, 473 K and 573 K (the curves were digitized from Fig. 2 of Ref. 28).
 336 **c** presents the position of the second, third and fourth neighbours as a function of pressure,
 337 as deduced from the peak positions of the PDF along the path P11. Panel **d** shows selected
 338 Raman spectra of liquid sulfur collected at the P,T points I,II and III of Fig.1. I: LDL
 339 below the λ -T. II: LDL above the λ -T. III: HDL.

340 **Extended Data Figure Legends**

341 **Extended Data Fig 1. Density discontinuity at 740 K.** Raw datasets of isothermal x-
 342 ray absorption profiles I/I_0 collected on decompression at 740 K. The black arrow
 343 indicates the density jump. B. Resulting isothermal density curve of sulfur in red and
 344 density variation of NaCl pressure standard in blue.

345 **Extended Data Fig 2. Structure factors $S(Q)$ of liquid sulfur collected on**
 346 **decompression along the isothermal path $T=740$ K.** The black arrow emphasizes the
 347 shift of the first peak position of $S(Q)$ at the HDL-LDL transition. The variation of the
 348 density calculated from the associated Pair Distribution Function (PDF) (black filled

349 squares) is presented in the inset panel together with the one obtained from the direct
350 density measurements (red empty squares).

351 **Extended data Fig 3. Isothermal density discontinuity.** Density of liquid sulfur as a
352 function of temperature along isobaric paths P9 at 0.4 GPa (left panel) and P10 at 1.3 GPa
353 (right panel).

354 **Extended Data Fig 4. Liquid-liquid critical point in sulfur. Panels a and b:** X-ray
355 absorption profiles I/I_0 in the horizontal and vertical directions in the vicinity of the
356 critical point. **Panels c and d:** Horizontal x-ray absorption profiles at temperatures
357 below (950 K) and above (1090K) the critical point. The red arrow in panel **c** indicates
358 the I/I_0 discontinuity at the liquid-liquid transition. No I/I_0 discontinuity is observed at
359 temperature above the critical point (panel **d**).

360

361 **Methods**

362 Methods are available in the Supplementary Information at <https://XXX>

363

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369 **Author contributions**

370 The original idea was defined by MM. The experiments were performed by LH, GG,
371 DS and MM with equal contributions. The data were analysed and the figures produced

372 by LH with contributions from all the co-authors. The manuscript was written by MM
373 and FD with contributions from all the co-authors.

374 Correspondence and requests for materials should be addressed to M. M.
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376 **Data Availability**

377 Tables containing the data points for all the main and extended data figures are provided
378 as Excel files. The data that support the findings of this study are available from the
379 corresponding author upon request.

380 **Competing interests**

381 The authors declare no competing interests.





